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Laboratory Procedures to Determine the Nitrogen Content of Solid Wastes

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Nitrogen becomes a significant solid waste parameter when it is evaluated in conjunction with two other parameters, namely carbon and hydrogen. The change in the C/N ratio of compost can be used to determine (1) the degree and rate of biological decomposition of organic matter in the compost, and (2) the suitability of the final product for use in agricultural soils. A knowledge of the nitrogen, carbon, and hydrogen contents of an incinerator's load and combustion products can also enable the engineer and scientist to (1) calculate the theoretical air requirements and combustion products, (2) formulate appropriate material and energy balance equations, and (3) evaluate and control effectively the efficiency of an incinerator system. To ensure the precise and accurate determination of the nitrogen content of solid wastes, investigations of the applicability of existing analytical procedures were conducted in this laboratory. Analysis of solid waste samples, containing up to 8 percent nitrogen, have demonstrated that the Kjeldahl-Wilfarth-Gunning-Winkler Method, the Comprehensive Nitrogen Method, and the Automated Dumas Method (as employed in the Coleman Nitrogen Analyzer) may be employed in the characterization of solid wastes. Detailed descriptions of these three methods are presented.

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LABORATORY PROCEDURES TO DETERMINE THE NITROGEN CONTENT OF SOLID WASTES

A Division of Research and Development
Open-File Report (RS-03-68-17)

written by
W. H. KAYLOR, Chemist, and N. S. ULMER, Research Chemist

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LABORATORY PROCEDURES TO DETERMINE THE NITROGEN CONTENT OF SOLID WASTES

A Division of Research and Development Open-File
Report prepared by W. H. Kaylor, Chemist,* and
N. S. Ulmer, Research Chemist

INTRODUCTION

Discussion

Nitrogen becomes a significant solid waste parameter† when it is evaluated in conjunction with two other parameters, namely carbon and hydrogen. The change in the C/N ratio of compost can be utilized to determine (1) the degree and rate of biological decomposition of organic matter in the compost[1,2] and (2) the suitability of the final product for use in agricultural soils.[3] A knowledge of the nitrogen, carbon, and hydrogen contents of an incinerator's load and combustion products can also enable the engineer and scientist to (1) calculate the theoretical air requirements and combustion products, (2) formulate appropriate material and energy balance equations, and (3) evaluate and control effectively the efficiency of an incinerator system.[4]

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*Mr. Kaylor is now serving with the National Field Investigations Center, Federal Water Quality Administration, U. S. Department of the Interior.

†In this paper the term parameter denotes a variable or characteristic of interest.

To ensure the precise and accurate determination of the nitrogen content of solid wastes, investigations of the applicability of existing analytical procedures were conducted in our laboratory. Analyses of solid waste samples, containing up to 8 percent nitrogen, have demonstrated that the Kjeldahl-Wilfarth-Gunning-Winkler Method, the Comprehensive Nitrogen Method, and the Automated Dumas Method (as employed in the Coleman Nitrogen Analyzer) may be employed in the characterization of solid wastes.[5] Detailed descriptions of these three methods are presented in the following sections.

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KJELDAHL-WILFARTH-GUNNING-WINKLER METHOD

Discussion

The Kjeldahl-Wilfarth-Gunning-Winkler Method,*,[1-5] may be employed to characterize solid waste samples if their nitrogen content is primarily organic and/or ammoniacal. Since the method will not recover nitrate nitrogen quantitatively, its applicability is presently limited to the analysis of municipal refuse, unfortified compost, incinerator residue, and other samples with little, if any, nitrate content. (Either the Comprehensive Nitrogen Method or the Automated Dumas Method should be employed to determine the total nitrogen content of samples containing significant quantities of nitrate, e.g. fortified compost, or samples of unknown nitrate concentration.)

In the Kjeldahl-Wilfarth-Gunning-Winkler method a sample is first digested with sulfuric acid. To increase the speed of the reaction and ensure the digestion of substances whose decomposition temperatures are above the boiling point of sulfuric acid, mercuric oxide and potassium sulfate are added. After the digestion has been completed, the mixture is then treated with alkaline sodium thiosulfate which destroys the mercuro-ammonium complex and permits the distillation of ammonia into 4 percent boric acid. A titration of the ammonium borate with standard sulfuric acid then permits the calculation of the total organic and ammoniacal nitrogen content of the sample.

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*See Appendix for a Brief History of the Kjeldahl Method.

Safety Precautions

1. Safety glasses should always be worn by the analyst while handling concentrated sulfuric acid and digestion mixtures.
2. The analyst should exercise care in weighing, transferring, and disposing mercuric oxide as inhalation, ingestion, or contact with the compound may cause mercurial poisoning.
3. Exhaust hoods (or special traps) should be employed during sample digestion to minimize the analyst's exposure to the evolving fumes.

Equipment

1. Apparatus, Kjeldahl. Digestion and Distillation, with (a) 6-heater unit, either gas or electric, capable of bringing 250 ml of water at 25 C to a rolling boil in 5 minutes, (b) block tin condensers enclosed in a copper coated cooling tank, and (c) pyrex delivery tubes. (Individual pyrex condensers and appropriate adapters may be substituted).
2. Balance, analytical, 0.1 mg readability
3. Bottle, dropper, pyrex, 250 ml
4. Bottles, reagent, pyrex, 1 liter and 2 liter
5. Bulbs, connecting, cylindrical or spherical trap style, pyrex, 5 to 6 cm in diameter
6. Buret, pyrex, 25 ml, graduated in 0.1 ml divisions
7. Carrier, designed to hold six 800-ml Kjeldahl digestion flasks (e.g., Fisher Scientific Co., Catalogue #10-114*)

*Product (or manufacturer) identification in this laboratory procedure does not imply endorsement by the U. S. Public Health Service.

8. Desiccator, large, either pyrex or stainless steel cabinet type
9. Dispensers delivery head, with S 24/40 joint, 25 ml and 40 ml (available from California Laboratory Equipment Company, 1165 67th Street, Oakland, California 94608)
10. Flasks, Erlenmeyer, pyrex, with S 24/40 mouth, 500 ml
11. Flasks, Erlenmeyer, pyrex, wide mouth, 500 ml
12. Flasks, Kjeldahl, for digestion and distillation, pyrex, 800 ml
13. Hood, exhaust and special stack to outside for venting fumes during the digestion of samples
14. Stoppers, rubber, sixe 7, for connecting bulbs to digestion flasks
15. Tubing, rubber, thin wall, for connecting bulbs to condensers and cooling tank to cold water supply and sink drain

Reagents

The chemicals in the following list should all be reagent grade and nitrogen-free.

1. Sucrose
2. Acetanilide
3. Disodium ethylenediaminetetraacetic acid (Disodium EDTA)
4. Hengar granules, plain
5. Potassium nitrate
6. Mercuric oxide
7. Sulfuric acid, concentrated (95 to 98 percent)
8. Silicone antifoaming agent: General Electric No. 66 or Do. Corning Antifoam Q
9. Zinc metal, granulated

10. Alkaline thiosulfate solution: Dissolve 450 g sodium hydroxide in approximately 700 ml distilled water, cool, add 80 g sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$), mix, and dilute with distilled water to 1 liter.

11. Boric acid solution: Dissolve 40 g boric acid in distilled water and dilute with same to 1 liter.

12. Methyl purple solution (indicator): Dissolve 0.3125 g methyl red and 0.2062 g methylene blue in distilled water (or 0.1 percent ethyl alcohol) and dilute with same to 250 ml.

13. Sulfuric acid standard solution, 0.1 N: Dissolve approximately 3 ml of concentrated sulfuric acid in 800 ml distilled water and dilute with same to 1 liter. Determine the normality of the solution using a primary standard, such as sodium borate.

Technique Evaluation

Before initiating the characterization of solid waste samples, the investigator should evaluate his technique by analyzing compounds of known nitrogen content. Either 0.25 g acetanilide or 0.5 g disodium ethylenediaminetetraacetic acid may be utilized as a standard sample. (See section on Precision and Accuracy.)

Solid Waste Sample Preparation

A solid waste sample must undergo physical preparation before its characterization is initiated in the laboratory. First, it must be dried to constant weight preferably in a forced-air (or mechanically convected)

oven. A temperature of 70 to 75 C should be utilized to dry municipal refuse or compost; incinerator residue may be dried at 100 to 105 C. The particle size of the dried sample should then be reduced to 2 mm or less using a hammermill, pulverizer, and/or laboratory mill. To assure sample homogeneity the ground components should be thoroughly mixed. Finally, since samples may absorb moisture during the grinding and mixing processes, they should be redried for four hours at the previously specified temperature and then stored in a desiccator until the analyses are completed.

Sample Analysis

The nitrogen contents of standard and solid waste samples should be determined in triplicate by the following laboratory procedure. A reagent blank, containing 2 g sucrose, previously dried at 105 C for 1 hour, should also be analyzed with each set of samples. In this manner any nitrogen present in the reagents will be detected, thus enabling the analyst to make appropriate corrections in the calculation of the nitrogen contents of the standard and solid waste samples.

Procedure	Comments
1. Weigh out approximately 2 g sucrose and transfer to a 800 ml Kjeldahl digestion flask, labelled "Blank."	1. Glassine paper, employed to support a sample during weighing and transferring, must not be added to the digestion flask.

2. Accurately weigh out three 1.0-to 2.5-g prepared solid waste samples and/or three standard samples (quantities previously specified) and transfer each to a labelled 800-ml Kjeldahl digestion flask.	2. An analytical balance must be employed.
3. To each flask add 16 g potassium sulfate, 0.7 g mercuric oxide, 25 ml concentrated sulfuric acid, and a few plain Hengar granules.	3. A larger volume of acid will be required if the sample weight exceeds that recommended.
4. To the "blank" flask add three drops of silicone antifoaming agent.	
5. Place the flasks on the heating apparatus in an inclined position.	5. The carrier may be utilized to support the flasks during transfer.
6. Gently heat the contents of each flask until frothing ceases; boil briskly until	6. The heaters should be previously adjusted to bring 250 ml water at 25C to a rolling

the solution clears and then for at least 30 minutes longer. (Samples containing organic material will require a 2-to 3-hour digestion.)

7. While the digested samples are cooling, align a 500-ml erlenmeyer flask, containing 50 ml boric acid, under each condenser to be employed during the distillation of ammonia from the samples.
8. To each cooled sample add 200 ml distilled water and mix. Then add 0.5 g zinc and mix again.
9. Pour 75 ml alkaline thiosulfate solution down the side of each flask and quickly attach a trap-condenser apparatus. Mix the contents of each flask and distill until the total

boil in 5 minutes. Test heaters after pre-heating 10 minutes if gas or 30 minutes if electric. Use 3 or 4 boiling chips to prevent superheating of the water.

7. The tip of the condenser delivery tube must be beneath the surface of the boric acid solution to prevent the escape of ammonia.

9. (a) CAUTION: The heaters should be turned on before connecting the flasks to the trap-condenser apparatus. This will minimize the danger of liquid sucking back through the condenser.

volume of the contents of the receiving flask is 200 ml (50 ml boric acid solution plus 150 ml distillate)

10. Add four drops of the methyl purple solution to each erlenmeyer flask and titrate the contents with the standard 0.1 N sulfuric acid solution to a light violet color. Record the ml of sulfuric acid employed for each sample.

11. Calculate the percent nitrogen in each standard or solid waste sample as described in the following section.

(b) Immediately after mixing, lower the erhlenmeyer flask containing the boric acid solution, so that the condenser delivery tube will drain and the pressure in the distillation flask will equalize.

10. The color of the solution will change from green to light gray and finally to light violet.

Calculations

The percent nitrogen in the samples should be calculated using the following formula:

$$\% \text{ Nitrogen} = \frac{(A-B)\ (N)\ (14)\ (100)}{C}$$

where A = ml 0.1 N sulfuric acid employed in the titration of the standard or solid waste sample

B = ml 0.1 N sulfuric acid employed in the titration of the blank

N = normality of the standard sulfuric acid solution

C = mg of standard or solid waste sample employed

Example:

$$\% \text{ Nitrogen} = \frac{(12.61-0.30)\ (0.1040)\ (14)\ (100)}{1016} = 1.76$$

Accuracy and Precision

Analyses of acetanilide or disodium ethylenediaminetetraacetic acid samples, containing 50 mg or less nitrogen, always yielded 98.5 or more percent nitrogen recovery. If lower recoveries are observed, the analyst's technique should be suspected.

The reproducibility of this method has been determined by calculating the standard deviation of replicate determinations of the nitrogen contents of various standard and solid waste samples. The data is presented in Table 1.

TABLE 1

THE PRECISION OF THE METHOD

Sample Identity			Number of replicate determinations per sample	Observed mean percent nitrogen	Standard deviation
Type	Source	Lab #			
Standards:					
Acetanilide			6	10.20	0.03
Disodium EDTA			11	7.41	0.07
Solid wastes*:					
Municipal refuse	Cincinnati	1†	12	1.07	0.05
"	Johnson City	6	6	1.01	0.05
"	New York	RSL208‡	8	2.36	0.02
Compost	Johnson City	W21B-D0	4	0.52	0.02
"	"	W16B-D7	4	0.83	0.05
"	"	W11B-D14	4	0.70	0.03
"	"	W6B-D22	4	0.78	0.03
"	"	W1B-D28	4	0.72	0.00
"	"	W30A-D35	4	1.02	0.04
"	"	W25A-D42	4	0.83	0.03
"	"	X-D70	4	0.71	0.03
"	"	X-FP	8	0.96	0.12
"	"	W25D-SL-DL	6	0.88	0.02
Incinerator residue	Cincinnati	RB-1	8	0.26	0.02
"	"	RB-2	8	0.34	0.02
"	New York	RSL-205	6	0.75	0.04
"	"	RSL-205-80M	3	0.87	0.01

*Glass and metals removed from samples before analyses initiated.
†The sample consisted primarily of dirt, leaves and wood.
‡The sample consisted primarily of food wastes.

References

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THE COMPREHENSIVE NITROGEN METHOD

Discussion

In 1967 the Comprehensive Nitrogen Method (CNM), a modification of the Kjeldahl Method*, was proposed by Gehrke et al.[1] for the determination of the nitrogen content of fertilizers, especially those containing high chloride-nitrate ratios. Subsequent investigations in our laboratory have demonstrated the applicability of the method in the determination of the total nitrogen (ammoniacal, organic, and nitrate) contents of municipal refuse, compost and incinerator residue.[2]

A sample of solid waste is first heated with metallic chromium in an acid medium to reduce the nitrates. The mixture is then digested with sulfuric acid. To increase the speed of the reaction and assure the digestion of substances whose decomposition temperature is above the boiling point of sulfuric acid, mercuric oxide and potassium sulfate are added. After the digestion is completed, the mixture is treated with alkaline sodium thiosulfate which destroys the mercuro-ammonium complex and permits the distillation of ammonia into 4 percent boric acid. A titration of the ammonium borate with standard sulfuric acid then enables the analyst to calculate the total (ammoniacal, organic, and nitrate) nitrogen content of the sample.

Safety Precautions

1. Safety glasses should always be worn by the analyst while handling concentrated sulfuric acid and digestion mixtures.

*See Appendix for A Brief History of the Kjeldahl Method.

2. The analyst should exercise care in weighing, transferring, and disposing mercuric oxide as inhalation, ingestion or contact with the compound may cause mercurial poisoning.
3. Exhaust hoods (or special traps) should be employed during sample digestion to minimize the analyst's exposure to the evolving fumes.

Equipment

The equipment, required for the determination of nitrogen in solid wastes by the Comprehensive Nitrogen-Method, is identical to that described in the Kjeldahl-Wilfarth-Gunning-Winkler Method (see p. 4-5).

Reagents

The chemicals in the following list should all be reagent grade and nitrogen-free:

1. Sucrose
2. Acetanilide
3. Disodium ethylenediaminetetraacetic acid (Disodium EDTA)
4. Potassium nitrate
5. Chromium metal, powder, 100 mesh
6. Hydrochloric acid, concentrated
7. Potassium sulfate
8. Mercuric oxide
9. Norton Alundum - 14 x
10. Sulfuric acid, concentrated (95 to 98 percent)

11. Silicone antifoaming agent: General Electric No. 66 or Dow Corning Antifoam Q

12. Zinc metal, granulated

13. Alkaline thiosulfate solution: Dissolve 450 g sodium hydroxide in approximately 700 ml distilled water, cool, add 32 g sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) and dilute with distilled water to one liter. (The concentration of sodium thiosulfate has been decreased from 160 g/liter to 32 g/liter to permit the addition of a larger volume of the solution [or quantity of alkali] without increasing the quantity of thiosulfate utilized to precipitate the mercury.)

14. Boric acid solution: Dissolve 40 g of boric acid in distilled water and dilute with same to 1 liter.

15. Methyl purple solution (indicator): Dissolve 0.3125 g methyl red and 0.2062 g methylene blue in distilled water (or 0.1 percent ethyl alcohol) and dilute with same to 250 ml.

16. Sulfuric acid standard solution, 0.1 N: Dissolve approximately 3 ml concentrated sulfuric acid in 800 ml distilled water and dilute with same to 1 liter. Determine the normality of the solution, using a primary standard such as sodium borate.

Technique Evaluation

Before initiating the characterization of solid waste samples, the investigator should evaluate his technique by employeing the procedure in the analyses of compounds of known nitrogen content. A small quantity of an individual substance, such as 0.25 g acetanilide, 0.5 g disodium

ethylenediaminetetraacetic acid, or 0.25 g potassium nitrate, may be employed as a standard, but a mixture of either the aforementioned quantities of acetanilide and potassium nitrate or disodium EDTA and potassium nitrate is preferable. (See section on Precision and Accuracy.)

Solid Waste Sample Preparation

A solid waste sample should be prepared as described previously in the Kjeldahl-Wilfarth-Gunning-Winkler Method (see p. 6-7).

Sample Analysis

The nitrogen contents of standard and solid waste samples should be determined in triplicate by the following laboratory procedure. A reagent blank, containing 2 g sucrose, previously dried at 105 C for 1 hour, should also be analyzed with each set of samples. In this manner any nitrogen present in the reagents will be detected, thus enabling the analyst to make appropriate corrections in the calculation of the nitrogen contents of the standard and solid waste samples.

Procedure	Comments
1. Weigh out approximately 2 g sucrose and transfer to a 800-ml Kjeldahl flask, labelled "Blank."	1. Glassine paper, employed to support a sample during weighing and transferring, must not be added to the digestion flask.

2. Accurately weigh out three 0.75-to 1.0-g, prepared solid waste samples and/or three standard samples (quantities previously specified) and transfer each to a labelled 800-ml Kjeldahl digestion flask.	2. An analytical balance must be employed.
3. To each flask add 1.2 g chromium and 35 ml distilled water. Let stand 10 minutes with occasional swirling.	3. Swirling will ensure solution of all the nitrate present.
4. Then add 7 ml concentrated hydrochloric acid to each flask. Let stand until a visible reaction occurs.	4. (a) Add a few drops of antifoaming reagent if foaming is anticipated. (b) Allow 1 to 5 minutes for reaction.
5. Transfer each flask to a burner and heat its contents to a rolling boil. (Maximum heating period is 5 minutes.) Remove from the burner and cool.	5. (a) The carrier should be utilized to transport the flasks. (b) The burners should be previously adjusted to bring 250 ml water at 25 C

	to a rolling boil in 5 to 7.5 minutes. Test heaters after preheating them 10 minutes if gas or 30 minutes if electric. Use 3 or 4 boiling chips to prevent superheating of the water.
6. Add 22 g potassium sulfate, 1.0 g mercuric oxide, and 1.5 g alundum to each sample.	
7. Transfer the flasks to the hood and add 25 ml concentrated sulfuric acid to each.	7. Additional sulfuric acid will be required if the quantity of sample exceeds that recommended.
8. Add three drops of the antifoaming reagent to the blank and any other sample containing considerable organic material.	
9. Place each flask on a preheated burner, adjusted to give a 5- to 7.5-minute boil test, and digest the sample for 1 to 1-1/2 hours	9. (a) See the burner adjustment described in comment 5 b. (b) The use of a preheated burner minimizes foaming at this stage.

with occasional gentle swirling.

(c) It should take 15 to 20 minutes for the copious white fumes to clear out of the bulb of the flask. Most samples should then be digested for an additional 30 minutes. If organic material, containing refractory nitrogen is present, digest for a total of 60 minutes after the white fumes have evolved from the flask.

10. While the digested samples are cooling, align a 500-ml erlenmeyer flask, containing 50 ml boric acid, under each condenser to be employed during the distillation of ammonia from the samples.

10. The tip of the condenser delivery tube must be beneath the surface of the boric acid solution to prevent the escape of ammonia.

11. To each cooled sample add 200 ml distilled water and mix. Then add 0.5 g zinc and mix again.

12. Pour 125 m' alkaline thiosulfate solution down the side of the flask and quickly attach a trap-condenser apparatus. Mix the contents of each flask and distill until the total volume of the contents of the receiving flask is 200 ml (50 ml boric acid plus 150 ml distillate).	12. (a) The heaters should be turned on before connecting the flasks to the trap-condenser apparatus. This will minimize the danger of liquid sucking back through the condenser. (b) Immediately after mixing, lower the erlenmeyer flask containing the boric acid solution, so that the condenser delivery tube will drain and the pressure in the distillation flask will equalize.
13. Add four drops of methyl purple to each erlenmeyer flask and titrate the contents with the standard 0.1 N sulfuric acid solution to a light violet color. Record the ml of sulfuric acid employed for each sample.	13. The color of the solution will change from green to light gray and finally to light violet.

14. Calculate the percent nitrogen in each standard or solid waste sample as described in the following section.

Calculations

The percent nitrogen in the samples should be calculated using the following formula:

$$\% \text{ Nitrogen} = \frac{(A-B)\ (N)\ (14)\ (100)}{C}$$

where A = ml 0.1 N sulfuric acid employed in the titration of the standard or solid waste sample

B = ml 0.1 N sulfuric acid employed in the titration of the blank

N = normality of the standard sulfuric acid solution

C = mg of standard or solid waste sample employed

Example

$$\% \text{ Nitrogen} = \frac{(12.61-0.30)\ (0.1040)\ (14)\ (100)}{1016} = 1.76$$

Accuracy and Precision

Analyses of acetanilide, disodium EDTA, potassium nitrate samples, containing less than 60 mg nitrogen, always yielded 98.2 or more percent nitrogen recovery. If lower recoveries are observed, the analyst's technique should be suspected.

The reproducibility of the method has been determined by calculating the standard deviation of replicate determinations of the nitrogen contents of various standard and solid waste samples. The data is presented in Table 1.

TABLE 1

THE PRECISION OF THE METHOD

Sample Identity			Number of replicate determinations per sample	Observed mean percent nitrogen	Standard deviation
Type	Source	Lab #			
Standards:					
Acetanilide			6	10.27	0.04
Disodium EDTA			11	7.39	0.09
Potassium nitrate			11	13.64	0.09
Solid wastes*:					
Municipal refuse	Cincinnati	5†	8	0.32	0.01
"	Johnson City	6	6	0.94	0.04
"	New York	RSL-208‡	10	2.37	0.04
"	Memphis	RSL-294	8	0.87	0.04
"	Ogden	RSL-12	6	0.53	0.04
Compost	Johnson City	W25D-SL-D1	6	0.93	0.01
"	St. Petersburg	SPF	6	1.03	0.05
"	"	SPF-Fort.	6	8.02	0.14
"	Jamaica	JAM	6	0.52	0.04
Incinerator residue	Cincinnati	RB-2	6	0.32	0.02
"	Memphis	RSL-292C	6	2.49	0.02
"	"	RSL-292I	6	0.04	0.01
"	Ogden	RSL-17	5	0.08	0.01
"	New York	RSL-205	8	0.74	0.03

*Glass and metals removed from samples before analyses initiated.
†This was a simulated sample.
‡This sample consisted primarily of food wastes.

References

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2. Ulmer, N. S. and W. H. Kaylor. An evaluation of the applicability of three methods for the determination of nitrogen in solid wastes. Cincinnati, U. S. Department of Health, Education, and Welfare. (In preparation)

THE AUTOMATED DUMAS METHOD

Discussion

In 1960 G. M. Gustin described a simple automatic apparatus for the rapid determination of nitrogen by the Dumas procedure.[1] Shortly thereafter the Coleman Instrument Corporation manufactured an instrument, capable of the automatic analysis of grain, fertilizers, soils, meat products, feeds, biological materials, and other substances dissociable at temperatures under 1100 C. Investigators in our laboratory have demonstrated that the Coleman Nitrogen Analyzer II, Model 29A*, (See figure 1) may also be employed successfully in the characterization of municipal refuse, compost, and incinerator residue.[2]

A 100-mg (or less), dry, homogenous solid waste sample is first packed in a combustion tube. After the tube has been inserted in the combustion train, high purity carbon dioxide is employed to purge the system of entrapped air. The sample is then decomposed at 850 to 900 C in the presence of oxidizing agents, such as Cuprox® (copper oxide) and Coboxide ® (cobalt oxide). The gaseous combustion products (nitrogen, nitrogen oxides, methane, carbon monoxide, and carbon dioxide) are swept along through the system by the flow of high-purity carbon dioxide. A platinum catalyst, mixed with the Cuprox® packed in the combustion and post-heater tubes, assures the complete combustion or oxidation of methane and carbon monoxide. The reduction of the nitrogen oxides to gaseous nitrogen is effected by the Cuprin® (reduced copper), in the post-heater tube. The gaseous mixture, flowing

*Product (or manufacturer) identification in this laboratory procedure does not imply endorsement by the Public Health Service.

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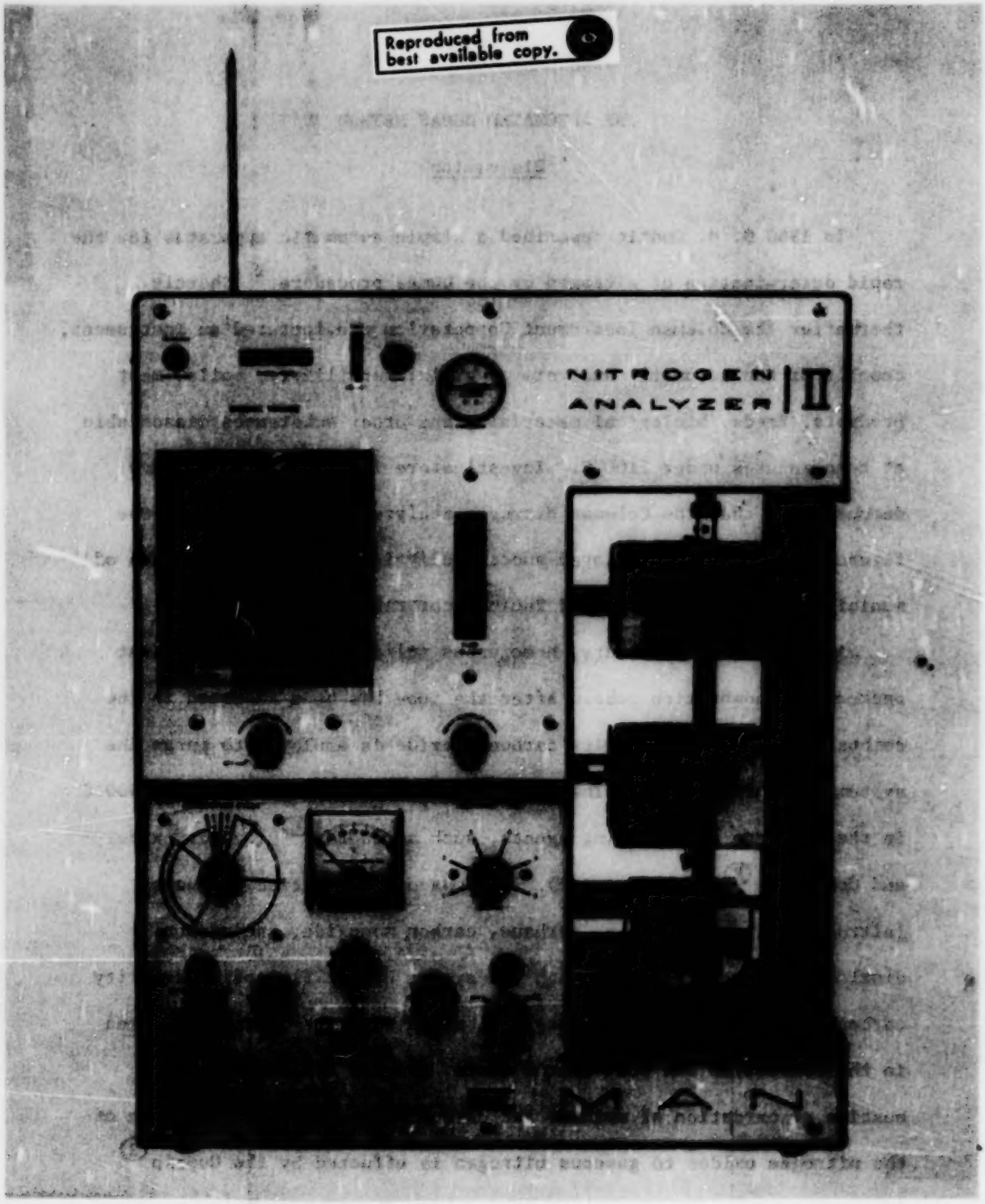

Figure 1. Coleman Nitrogen Analyzer II, Model 29A
(Courtesy, Coleman Instruments Division of the
Perkin-Elmer Corporation.)

from the latter tube, is then scrubbed thoroughly in a caustic solution to remove all its carbon dioxide content. The remaining nitrogen is collected and measured in a 50,000-µl stainless steel syringe linked to a digital counter. Since the purging, combusting and sweeping actions are entirely automatic, a sample analysis can be performed with ease in 15 minutes.

Safety Precautions

1. The analyst should wear cotton gloves while handling the cold combustion or post-heater tubes. (Observations in our laboratory have indicated that the tube durability, and hence procedural safety, may be decreased by repeated alternate exposures of the tube to perspiring hands and furnace temperature.)
2. During the analysis of substances which pyrolyze rapidly or detonate, a protective shield should be attached to the side of the instrument and positioned in front of the combustion tube. If a shield is temporarily unavailable, safety glasses should be worn to protect the eyes.
3. The temperature of the combustion tube furnaces should always be maintained below 1020 C to prevent the sintering of the Cuprox® tube packing and the possible explosion of the combustion tube.
4. The analyst should always remove a hot combustion tube from the train by carefully grasping the cooler ends of the tube. NEVER grasp the hot center of the tube.

5. The analyst should wear an asbestos glove when inserting his hand into the muffle furnace to mix or remove the Cuprox® - Platinum catalyst reagent, being regenerated at 800 C.

Equipment

Requirements

1. Analyzer, Nitrogen II, Coleman Model 29A, complete with nitrometer (Coleman #29-312); three Vycor® combustion tubes (Coleman #29-328); Vycor(R) post-heater tube (Coleman #29-337); special scale thermometer (Coleman #29-340); 1 package of 100 disposable aluminum combustion boats (Coleman #29-412); four Neoprene® compression washers (Coleman #9584-V); two combustion tube plugs (Coleman #9595V); copper gas supply tubing, 60-inches long, with compression fitting and bushing at one end to fit regulator outlet valve (Coleman #3825V); two spring-loaded, joint-type pinch clamps (for nitrometer connections); a three wire cord and three blade plug (for operation on 115 volts, 50/60 cycle, 750 watts); Operating Directions D360-C (Coleman #29-904) and reagents #4,5,6,8 and 10, listed in the next section.
2. Balance, analytical, readability 0.0001 g
3. Barometer, accurate, readability 0.5 mm Hg
4. Desiccator, large, either pyrex or stainless steel cabinet type
5. Dishes, evaporating, porcelain (These are used to support the Cuprox® Platinum Catalyst reagent while it is being regenerated. The size of the dishes will therefore depend upon the inner dimensions of the muffle furnace.)

6. Furnace, muffle, capable of maintaining 800 C for a two-hour period
7. Gloves, asbestos, 14 inches long
8. Gloves, cotton, large (These are available from either Davis Gloves, Springfield, Ohio, or Wash Rite, Inc., 1410 Cornell, Indianapolis, Indiana.)
9. Mats, asbestos, 1/8 by 12 by 12 inches (These are used to support the hot evaporating dishes after they are removed from the furnace.)
10. Rack, aluminum (or cadmium-plated) for holding combustion tubes
11. Regulator, two stage, Coleman type for Coleman Nitrogen Analyzer, with CGA connection #320 (Model 8C, Mathieson Scientific Company, #26285-05)
12. Rod, stirring, teflon-coated, 15 inches long, 1/4 inch in diameter
13. Screw driver, slot drive, blade 1/4 inch wide, 6 to 10 inches long
14. Shield, protective, for use in combustion of substances that pyrolyze rapidly or detonate (Coleman #33-450)
15. Sieve, brass, 8 inch, US #40
16. Sieve cover and receiver, brass, 8 inch
17. Spatula, stainless steel, rounded and pointed blades, micro
18. Support, gas cylinder
19. Tongs, crucible type, nickel plated steel, 18 inches long
20. Tweezers, 4-1/2 inches long, for grasping boats
21. Wool, glass
22. Wrench, open end, 1-1/8 inches, for installing pressure regulator on gas tank
23. Wrenches, 3/8, 7/16 and 1/2 inch, for connecting copper tubing to output of gas regulator and input fitting of instrument

Assembly and Maintenance

The Coleman Nitrogen Analyzer and its accessories should be assembled, evaluated, and maintained as described in the Operating Directions for the instrument.

Reagents

Requirements

1. Acetanilide, ACS reagent grade, crystalline
2. Carbon dioxide, Coleman instrument grade, 99.99 percent pure (cylinder size 1)
3. Causticon®, potassium hydroxide solution, 1 pint (Coleman #29-110)
4. Coboxide®, cobalt oxide, 30-g bottle (Coleman #29-170)
5. Cuprin®, metallic copper, 1-lb bottle (Coleman #29-120)
6. Cuprox®, copper oxide, fines, 1-lb bottle (Coleman #29-140)
7. Cuprox®- Platinum Catalyst Reagent, 5-lb bottle (Coleman #29-165)
8. Disodium ethylenediaminetetraacetic acid, ACS reagent grade, powder (Minimum assay: 99 percent)
9. Mercury, reagent, redistilled, 50 ml
10. Potassium nitrate, ACS, reagent grade
11. Salicylic acid, ACS, reagent grade, nitrogen free
12. Silica gel, indicating, mesh size 6-16, 5 lb unit
13. Silver vandanate, 40-g bottle (Coleman #33-130)

Preparation, Maintenance and Storage

All fresh reagents should be employed as received. The replacement, regeneration, and/or maintenance of the reagents should be accomplished as outlined in the Operating Directions for the instrument. All capped (but unsealed) reagent bottles, containing solids, should be stored in a desiccator to minimize the sorption of moisture.

Technique Evaluation

Before initiating the analysis of solid waste samples, the investigator should evaluate his technique by employing the procedure in the analyses of compounds of known nitrogen content. Either 0.05 g acetanilide or 0.10 g disodium ethylenediaminetetraacetic acid (disodium EDTA) should be utilized routinely as a standard sample. To evaluate the recovery of nitrate nitrogen, the analyst should use a 0.1 g-potassium nitrate sample to which an equal weight (i.e., 0.1 g) of nitrogen-free salicylic acid has been added. (See section on Accuracy and Precision.)

Solid Waste Sample Preparation

The procedure for the preparation of a solid waste sample is the same as that previously outlined in the Kjeldahl-Wilfarth-Gunning-Winkler Method (see p. 6-7) except that the sample's particle size should be reduced to 0.5 mm or less before the mixing is initiated.

Sample Analysis

The analyst should employ the following instructions in conjunction with the Sample Analysis procedures, outlined in the Operating Directions for the instrument:

1. All determinations (including blanks) should be performed in triplicate.
2. The sample should contain 100 mg (or less) organic matter and 40 mg (or less) nitrogen.
3. The combustion tube packing, employed in all analyses, should be modified by adding Cuprox® fines 1/4 inch below, 1/4 inch above and completely around the aluminum boat. This packing, if carefully performed, will prevent the fusion of the boat with the Vycor® combustion tube.
4. The instrument should be operated on the normal 12-minute cycle.
5. The furnace controls should be adjusted so that the post-heater tube furnace is maintained at 700 C and the lower and upper combustion tube furnaces attain 850 to 900 C during the final portion of the combustion period. (Occasionally, as in the analysis of the potassium-nitrate-salicylic acid standard mixture, the analyst may observe a sintering of the Cuprox® around the sample in the combustion tube. Lower combustion furnace settings should then be employed to minimize hazards and increase tube life.)
6. Daily furnace warm-up periods may be avoided by leaving the instrument in the "standby" position overnight. (The nitrometer must be disconnected as usual.)

Calculations

The percent nitrogen in a standard or solid waste sample should be determined as follows:

1. Record V_o, the observed volume of nitrogen (µl).

$$V_o = R_2 - R_1$$

where R_1 = the initial counter reading

R_2 = the final counter reading

2. Determine V_c, the corrected nitrogen volume (µl)

$$V_c = V_o - (V_b + V_t)$$

where V_b = volume of blank (µl)

V_t = volume correction for temperature (µl)

$= C_f (t_2 - t_1)$

where C_f = correction factor per degree Kelvin (Table I)

t_1 = the initial syringe temperature in degrees Kelvin

t_2 = the final syringe temperature in degrees Kelvin

3. Determine P_c, the corrected barometric pressure (mm Hg)

$$P_c = P_o - (P_b + P_v)$$

where P_o = the observed barometric pressure (mm Hg)

P_b = the pressure correction for temperature (Table II)

P_v = the pressure correction for the vapor pressure of potassium hydroxide (Table III)

4. Determine % N, the percent nitrogen, using the following formula:

$$\% N = \frac{P_c}{T} \times \frac{V_c}{W} \times 0.0449$$

where $T = t_2$, the final syringe temperature in degrees Kelvin

W = the sample weight in mg

TABLE I

CORRECTION FACTOR (C_f) EMPLOYED IN THE CALCULATION OF THE VOLUME CORRECTION FOR TEMPERATURE (V_t)*†

Final counter reading (ul)	C_f‡ (ul/K)	Final counter reading (ul)	C_f‡ (ul/K)
0	12	24,000	92
1,000	15	25,000	95
2,000	19	26,000	98
3,000	22	27,000	102
4,000	26	28,000	105
5,000	29	29,000	109
6,000	32	30,000	112
7,000	35	31,000	115
8,000	39	32,000	119
9,000	42	33,000	122
10,000	45	34,000	127
11,000	48	35,000	129
12,000	52	36,000	132
13,000	55	37,000	135
14,000	59	38,000	139
15,000	62	39,000	142
16,000	65	40,000	145
17,000	69	41,000	148
18,000	72	42,000	152
19,000	76	43,000	155
20,000	79	44,000	159
21,000	82	45,000	162
22,000	85	46,000	165
23,000	89	47,000	169

*Based on Coleman Instrument Corporation. D-360C Operating Directions for the Coleman Model 29A Nitrogen Analyzer. Maywood, Illinois. 1966, p. 22.

†$V_t = C_f (t_2 - t_1)$ where t_1 and t_2 are the initial and final temperatures, expressed in degrees Kelvin, respectively.

‡Factor applicable only for measurements made with nitrometers having check valves.

TABLE II

PRESSURE CORRECTION (P_b) FOR TEMPERATURE*

Room Temperature C	P_b (mm Hg)	
	P_o = 700 to 749†	P_o = 750 to 780†
10	1.2	1.3
15	1.8	1.9
20	2.3	2.5
21	2.4	2.6
22	2.5	2.7
23	2.7	2.9
24	2.8	3.0
25	2.9	3.1
26	3.0	3.2
27	3.1	3.3
28	3.3	3.5
29	3.4	3.6
30	3.5	3.7
31	3.6	3.8
32	3.7	3.9
33	3.9	4.1
34	4.0	4.2
35	4.1	4.3

*Based on Coleman Instrument Corporation. D-360C Operating Directions for the Coleman Model 29A Nitrogen Analyzer II. Maywood, Illinois, 1966, p. 22.

†P_o = observed barometric pressure in mm Hg.

TABLE III

PRESSURE CORRECTION (P_v) FOR VAPOR PRESSURE OF POTASSIUM HYDROXIDE*

Temperature† (K)	P_v (mm Hg)
288	4.1
293	5.7
298	7.4
299	7.8
300	8.3
301	8.7
302	9.2
303	9.6
304	10.2
305	10.8
306	11.3
307	11.9
308	12.5
309	13.3
310	14.1
311	14.9
312	15.7
313	16.5

*Based on Coleman Instrument Corporation. D-360C Operating Directions for the Coleman Model 29A Nitrogen Analyzer II. Maywood, Illinois, 1966, p. 22.

†For practical purposes the temperature of the potassium hydroxide is the same as that of the syringe.

Example:

If P_o = 747.2 mm Hg at 24.9C

W = 39.7

R_1 (Blank) = 5219

R_2 (Blank) = 5270

R_1 (Solid waste) = 5270

R_2 (Solid waste) = 5620

t_1 = 303.1

t_2 (or T) = 303.3

Then V_b (Blank) = 51

V_o (Solid waste) = 350

V_c (Solid waste) = 350 - [51 + (29) (303.3 - 303.1)]

= 293.2

P_c = 747.2 - (2.9 + 9.6)

= 734.7

$$\%N = \frac{734.7}{303.3} \times \frac{293.2}{39.7} \times 0.0449$$

= 0.80

Accuracy and Precision

Analyses of acetanilide, disodium ethylenediaminetetraacetic acid or potassium nitrate samples, containing less than 20 mg nitrogen, always yielded 99 or more percent nitrogen recovery. If lower recoveries are observed the analyst's technique should be suspected.

The reproducibility of the method has been determined by calculating the standard deviation of replicate determinations of various standards and solid waste samples. The data is presented in Table IV.

TABLE IV

THE PRECISION OF THE METHOD

Sample Identity Type	Source	Lab #	Number of replicate determinations per sample	Observed mean percent nitrogen	Standard deviation
Standards:					
Acetanilide			10	10.34	0.06
Disodium EDTA			14	7.56	0.02
Potassium nitrate			6	13.72	0.06
Solid wastes*:					
Municipal refuse	Cincinnati	5†	6	0.25	0.06
"	Johnson City	6	6	0.92	0.03
"	New York	RSL-208‡	6	2.44	0.06
"	Memphis	RSL-294	6	0.72	0.07
"	Ogden	RSL-12	10	0.49	0.06
Compost	Johnson City	W11B-D14	6	0.78	0.08
"	"	W25D-SL-D1	12	0.82	0.06
"	St. Petersburg	SPF	6	1.09	0.03
"	"	SPF-Fort.	10	8.16	0.10
"	Jamaica	JAM	9	0.57	0.05
Incinerator residue	Cincinnati	RB-2	5	0.28	0.03
"	Memphis	RSL-292C	6	2.55	0.06
"	"	RSL-292I	6	0.03	0.01
"	Ogden	RSL-17	6	0.08	0.01
"	New York	RSL-205	3	0.84	0.00

*Glass and metals removed from samples before analyses initiated.
†This was a simulated sample.
‡This sample consisted primarily of food wastes.

References

1. Gustin, G. M. A simple, rapid automatic micro-Dumas apparatus for nitrogen determination. Microchemical Journal, 4:43-54, 1960.

2. Ulmer, N. S. and W. H. Kaylor. An evaluation of the applicability of three methods for the determination of nitrogen in solid wastes. Cincinnati, U. S. Department of Health, Education and Welfare. (In preparation)

APPENDIX

A Brief History of the Kjeldahl Method

The historical background and evolution of the Kjeldahl method have been thoroughly reviewed by R. B. Bradstreet[1]. The following brief resume will hopefully afford the analyst a greater appreciation of the ingenuity and resourcefulness of the many scientists who contributed to the development of the method.

In 1883 Johann Kjeldahl, a Danish chemist associated with the Carlsberg Laboratory in Copenhagen, published a new method for the determination of nitrogen. The procedure, developed primarily to facilitate a study of the protein changes in grain, consisted of the heating of a sample for 2 hours in concentrated sulfuric acid to which fuming sulfuric acid and phosphoric anhydride had been added, subsequent oxidation with powdered permanganate, dilution and transferance of the mixture to a distillation flask, addition of alkali and then zinc, distillation of the ammonia into standard acid, addition of potassium iodide and iodate to the distillate, and finally a titration of the liberated iodine with standard thiosulfate.

Shortly after the publication of this method, Kjeldahl's contemporaries proposed numerous modifications and improvements. In 1885 Wilfarth reported that the speed of the digestion could be accelerated by the addition of a copper salt. He also described the catalytic effects of the oxides of copper, iron, mercury, bismuth, manganese, zinc and lead. Since mercuric oxide, the most effective catalyst, tended to form a complex with ammonia and thus lower nitrogen recovery,

its use was discontinued until chemists discovered that the complex could be destroyed by the addition of alkaline sulfide, thiosulfate, monosodium phosphate, potassium xanthanate, or potassium arsenate. In the years following Wilfarth's significant contribution, investigators have elucidated and established many other substances capable of accelerating specific digestion reactions. The addition of a catalyst has therefore become a routine and universally accepted step in the Kjeldahl procedure.

In 1889 J. W. Gunning reported that the addition of potassium sulfate to the digestion mixture would raise its boiling point, increase the severity of the reaction, shorten the digestion period, and hence permit the analyses of other types and sizes of sample. Although the applicability of many other salts has been evaluated since Gunning's observations were published, potassium sulfate is still recommended, particularly for the analysis of refractory compounds. The lower acid-salt ratios, attainable with this salt, have permitted digestion at higher temperatures without loss of nitrogen.

Although the suggestions of Wilfarth and Gunning greatly increased the scope of the Kjeldahl method, research has since demonstrated that nitro, nitroso, azo, aminoazo, and hydrazine compounds, and all others in which a nitrogen atom is linked to an oxygen atom (or atoms) or to a second nitrogen atom, must be reduced before their nitrogen contents can be recovered quantitatively. This reduction has been accomplished in two general ways: (1) as a pretreatment of the sample with substances such as powdered copper, zinc, chromium, titanous chloride, potassium

iodide, and sodium hydrosulfite, and (2) by the addition of compounds such as sucrose, benzoic acid, phenol, and salicylic acid directly to the acid and sample. The latter compounds supply a reducing effect during the Kjeldahl digestion as they decompose to free carbon with subsequent reduction of the sulfuric acid to sulfur dioxide.

Kjeldahl originally proposed that powdered potassium permanganate be added to the sample upon completion of the acid-digestion. Although he felt that this step was necessary to assure the complete oxidation or conversion of any nitrogen not previously converted to ammonium sulfate by the digestion, it was later discontinued when variations in nitrogen recovery were observed. During the 20th century other oxidizing agents such as hydrogen peroxide, perchloric acid, and potassium persulfate have occasionally been employed with more favorable results.

The procedure, proposed by Kjeldahl for the recovery of ammonia and the final determination of nitrogen, has also been modified by numerous investigators. If the ammonia is distilled, a direct heat distillation is usually employed; aeration and steam distillation techniques have been proposed however. Kjeldahl's time-consuming titration has been replaced either by a back titration with a known volume of standard acid or the direct titration of ammonium borate, as proposed by Winkler in 1913. Other methods, such as gravimetry, nesslerization, pH measurement, colorimetric reaction, or neutralization of the digest followed by direct estimation of the ammonia have also been utilized successfully in the analysis of samples.

Reference

1. Bradstreet, R. B. The Kjeldahl method for organic nitrogen. New York, Academic Press, 1965. 238 p.

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